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**The Replacement of Halogen by
Amino Groups in Chlor-Substituted Aromatic Compounds**

By

Armand James Quick

**A Thesis Submitted for the Degree of
Master of Science**

UNIVERSITY OF WISCONSIN

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History.

The stability of the halogen atom in the benzene ring has been of considerable interest because it has prevented, until recently, the direct synthesis of phenols and aromatic amino compounds from the halogen derivatives of aromatic hydrocarbons. The early investigators¹ failed entirely in their efforts to replace the halogen by other groups. It was not till 1914 that Meyer and Bergious² reported that a dilute solution of sodium hydroxide converts chlorobenzene almost quantitatively into phenol at 300°C., and that ammonia under similar conditions converts it partly into aniline.

It has long been known that certain negative groups, of which the nitro group is the best example, when in ortho or para position to the halogen atom have a marked labilizing effect on it. Engelhardt and Latchinow³ as early as 1870 reported that they were able to convert, at least partially, ortho and para nitrochlorobenzene into their respective nitranilines by heating with ammonia at 150°C. In 1908 the Aktien Gesellschaft fur Anilin Fabrikation⁴ took out a patent for the preparation of p. nitraniline by this process which probably is used to some extent at the present time. The conversion of trinitro-chlorobenzene into picric acid is another illustration of the labilizing effect of the nitro group which is of commercial significance.

¹ A. 104. p.225

A 121 258

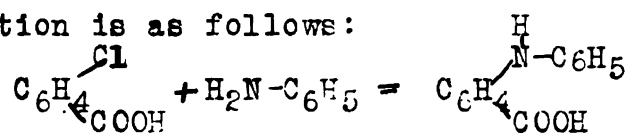
A 121 262

² Ber. 47 p.3165

³ Zeitsch Chem. 1870 p 3232.

⁴ D.R.P 148749

In 1903 Ullmann⁵ accidentally made the important discovery that metallic copper had a strong labilizing effect on nuclear halogen. While trying to condense o. benzoic acid with sodium phenate in the presence of finely divided copper, Ullmann incidentally used aniline as a solvent. Much to his surprise, the aniline entered into the reaction and o. phenylanthranilic acid was obtained. The reaction is as follows:



This discovery opened a new field of investigation. It was soon found that o. chlorbenzoic acid could be condensed with phenol⁶, thiophenol⁷, and similar compounds under the influence of finely divided copper. It was furthermore found that o. chlorbenzoic acid could be condensed with glycine⁸, with methylamine⁹, and other aliphatic as well as aromatic amines and amino compounds¹⁰ under the influence of this catalyst.

Almost all the early work was done on o. chlorbenzoic acid. This is due most likely to the fact that the work was started with that compound, and also because of its relation to anthranilic acid which is an important intermediate in the manufacture of indigo.

-
5. Ber. 36. p 2382
 6 Ber 37 853
 7 Ber 37 4526
 8 Lasser-Cohn's Arbeitsmethoden. (4 ed) p 601
 9 "
 10 I.D.R.P. No. 145189
 146102
 146950

Four years after Ullmann's discovery a series of patents appeared which dealt with the conversion of chlorosubstituted benzene derivatives into aromatic amino compounds by means of ammonia in the presence of copper salts. Among these patents were listed the preparation of aniline from chlorobenzene,¹¹ p.phenylenediamine from p,dichlorobenzene¹² and from p.chlor-aniline,¹³ p.phenylenediaminemonosulphonic acid from p,dichlor-sulphonic acid,¹⁴ and from the isomeric p.chlor anilinesulphonic acids,¹⁵ and p.aminophenol and some of its derivatives from p.chlor phenol and its corresponding derivatives¹⁶. There also appeared a patent for the preparation of diphenylamine from brombenzene.¹⁷ Cuprous iodide is used in the later patent, whereas in the other patents copper sulphate is used, the latter claiming that the cuprous iodide is a much more effective catalyst.

Very recently Kitamura¹⁸ reported that he prepared acetaminophenol ~~ethers~~ by condensing acid amides with halogen substituted phenol ~~ethers~~ in the presence of copper as well as zinc salts.

11. D.R.P.No. 204951

12 202171

13 204848

14 202564

15 202568

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16 205415

17 187870

18 J.Tokyo Chem Soc. 39 1121-30 (1918) J Pharm.
Soc. Japan 1918, No.442971.

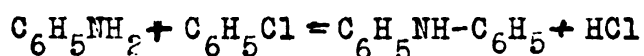
Problem.

The discovery of Ullmann has opened a wide field of investigation, but due to the fact that it had commercial possibilities it was soon buried in patents and so found little recognition in pure synthetic organic chemistry. The information concerning the reactions already mentioned is therefore very limited, consequently in this work an attempt is made to get some concrete information concerning them.

The particular reactions studied were those of ammonia on mono and p.dichlorobenzene. The object of the work was, first, qualitatively to see whether any appreciable reaction took place; secondly, quantitatively to determine the yields obtainable; thirdly to study the experimental difficulties in order to ascertain whether the method is feasible for synthesis; fourthly, to find the optimum conditions for the reaction. The work was carried out with mono and p.dichlorobenzene because these could readily be prepared pure and were least liable to enter into complicated side reactions with ammonia. P. dichlorobenzene, moreover, is a useless by-product in the preparation of chlorobenzene, whereas the phenyldiamine which can be prepared from it is a valuable compound. The reactions studied are primarily as follows:



There is a possibility of other reactions taking place. Thus, the aniline formed from chlorobenzene may react with second molecule of the same substance to form diphenylamine according to the following equation:



In the case of p.dichlorobenzene the possibilities are greater. One illustration will suffice. If only one chlorine atom is replaced by an amino group, p.chloranilin is formed, which can react with another molecule of p.dichlorobenzene to form dichlorodiphenyl amine, or it can react with a second molecule of p.chloraniline to form chlorphenyl-p.phenylenediamine.

Altho ammonia was used exclusively to remove the halogen, other reagents suggest themselves, such as sodamid, and zinc ammonium chloride. Then, too, the reaction of dilute solutions of sodium hydroxide, of ethyl alcoholate, and the like on chlor-substituted benzene could be studied with profit.

Experimental.

Apparatus used.

Pressure bomb or autoclave.

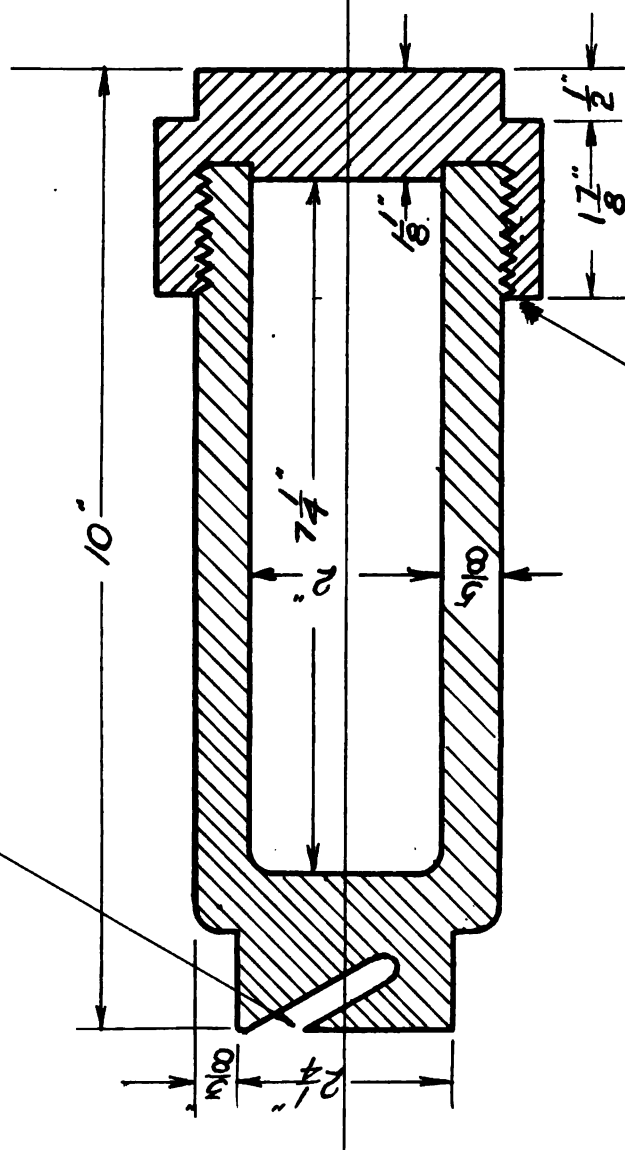
Since all the work was done under considerable pressures, it was necessary to have an autoclave that was strong enough to withstand at least 1000 pound of pressure to the sq. in. The early work was done in glass tubes, but these were found very unsatisfactory, for in the first place, it was not possible to work with large amounts of material, and in the second place, the loss of material due to blowing up of tubes was considerable.

The autoclave used for this work was made out of mild steel shafting, 3 1/4" 9" with a boring 2" in diameter and 7" deep, giving it a capacity of 350 cc and leaving the walls 5/8" thick. The tube was fitted with a screw cap. Permanite, an asbestos graphite packing, was used for a gasket with very satisfactory results. (See diagram)

Preparation of compounds used.

Monochlorobenzene. This compound was prepared by the method of Mouneyrat and Poucit. Ordinary commercial benzene was chlorinated by means of dry chlorine gas in the presence of anhydrous aluminum chloride acting as a catalyst. After passing in the theoretical amount of chlorine as determined by the increase in weight of the reaction mixture, the oily liquid was washed successively with dilute hydrochloric acid, with water, with dilute solution of sodium carbonate, and finally again with water, and then dried over fused calcium chloride. Upon fractionating, only a very small

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amount came over below 120° , indicating that little benzene was left. The fraction distilling between 127 and 140° was collected and redistilled, and the portion boiling from 131 - 134° was collected and used. The yields were poor, since only 800 grams of chlorbenzene were obtained from 2000 grams of benzene. Judging by the large amount of tarry and high boiling material obtained, it would seem that the aluminum chloride had also acted as a condensing agent (Friedel-Craft reaction) and so lessened the yield of chlorbenzene.

P.dichlorobenzene was obtained from the Dow Chemical Company, Midland, Mich. It was perfectly white and on refractionation practically all distilled at 170 - 171° . (unc)

Cuprous chloride. Merck's cuprous chloride was used. It had a greenish gray color showing that it contained a small amount of cupric chloride.

Cuprous iodide. This compound was prepared by adding potassium iodide to a saturated solution of copper sulphate. Cuprous iodide immediately separated out with the liberation of free iodine. The precipitate was filtered off and washed with alcohol to remove the iodine. The product was almost white.

Ammonia. The ordinary 28-28% ammonia reagent was used.

Study on catalysts.

The first problem in this work was to determine whether copper salts were the only substances that had labilizing affects on nuclear halogen. Among the substances that were used were salts of nickel, cobalt and zinc. These were used because they form complexes with ammonia that are similar to those of copper. Then, too, zinc has been reported to have catalytic properties in reactions similar to those mentioned. Since negative results were obtained in all cases, it can be concluded that the copper ammonium complex is not the cause for the catalytic action of copper. Ferrous sulphate, metallic mercury, mercuric chloride, sodium acid sulphite, uranium nitrate, and activated charcoal were also tried. The first three were used because they possess catalytic properties in other organic reactions, the sodium acid sulphite because of its well known power in aiding the conversion of b.naphthol into b.naphthylamine thru ammonia. In all cases the results were negative.

Since copper salts showed decided catalytic properties, it seemed advisable to study the relative activity of a number of them. For this study a series of tubes, each containing a different copper salt, were run under identical conditions. Each tube contained 5 grams of p.dichlorbenzene, 18 cc of concentrated ammonia, and .5 gram of the catalyst. The set was heated at 200-210 for 12 hours, and after cooling, the unaltered p.dichlorbenzene was filtered off and weighed, all other products of the reaction being water soluble.

The results were as follows:

Salt used.	P. dichlorbenzene unaltered.	
	In grams	In %
CuI	Tr.	-
CuCl	.15	3.0
CuCl ₂	.70	14.
CuSO ₄	1.15	23.

From this it can be seen that the cuprous salts are more active than the cupric. Indeed there is a probability that cupric salts only become active after reduction to the cuprous condition in the reaction mixture. This assumption seems to be born out experimentally, for on adding potassium permanganate which insures keeping the salt in the cupric condition, no reaction took place at all.

Cupric acetate and nitrate seem to have even less catalytic power than the sulphate altho these experiments were carried on under somewhat different conditions so that exact comparisons could not be made. Metallic copper, which was prepared by reducing finely divided copper oxide with hydrogen, had no catalytic effect whatsoever. This perhaps accounts for the fact that when powdered aluminum was added to the reaction mixture containing a copper salt, no conversion took place of the dichlorbenzene. Iron filings used with the copper salt did not stop the reaction but considerably retarded it.

The effect of solvents on the reaction was not studied very extensively. Almost all of the reactions were carried out in aqueous solutions altho in a few cases alcohol was employed as a solvent. The alcohol was saturated with dry ammonia gas and the p.d.

chlorobenzene and cuprous chloride added as in the other experiments. Since not a trace of p.phenylenediamine was produced, it seems that catalytic action of the copper salts is limited to aqueous solutions.

Conversion of p.dichlorobenzene into p.phenylenediamine .

In studying the reaction for the conversion of p.dichlorobenzene into p.phenylenediamine, the first and most important problem that came up was the isolation and identification of the latter product. Since the literature states that the free base is very soluble in ether, the first method that suggested itself was the extraction with ether. The method was a failure, for in the first place, only part of the base could thus be shaken out, and, furthermore, the product obtained was contaminated with oily non-crystalline impurities that were hard to remove. It was, furthermore, observed that ether which had been exposed to light and air for some time oxidized the base to a dark colored oil. This is due to the peroxides that old ether contains. Benzene and ethyl acetate were found to be slightly better solvents, but not good enough to make it a feasible method.

The next method tried was the precipitation of the free base by concentrating the solution under reduced pressure. A black amorphous precipitate containing a small amount of a crystalline substance was obtained. The mass was dried and extracted with ether whereupon a small amount of the base was obtained; the yields however were poor.

The most successful extraction scheme consisted in mixing

the crude hydrochloride of p.phenylenediamine with either lime or caustic soda, and extracting the mixture with benzene in a Soxhlett Extractor. The product consisted of reddish crystals which were easily purified by sublimation. The pure product consisted of perfectly colorless plates which had a melting point of 138-139° (uncor), whereas the corrected melting point is 140°. These crystals also gave the characteristic color test of p.phenylenediamine,¹⁹ which is as follows: A drop of ferric chloride added to a dilute solution of the base or its hydrochloride will produce a deep green color which in a few seconds changes to a characteristic violet. With more concentrated solutions and boiling, a brown solution is obtained and the odor of quinone can be detected.

It can readily be seen that the extraction methods are not very satisfactory. The next step was to try distillation methods. Ledoux²⁰ reports that when a mixture of phenylenediamine hydrochloride and anhydrous sodium carbonate are dry distilled, theoretical yields of p.phenylenediamine are obtained. This experiment was tried out and found far less satisfactory than one would expect from Ledoux's statement, due to the experimental difficulties that one encounters. In the first place, water is always given off even after the mixture has been dried at 110° for a considerable time, and this water at the high temperature causes discoloration probably by inducing oxidation. In spite of Ledoux's statement, it was found that decomposition takes place, and a basic gas is invariably formed which indicates a breaking up of the p.phenylenediamine. The yields were poor. Substituting sublimation for distill-

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20. B. 7. p.153

ation, much better results were obtained, and with additional improvements on the sublimation apparatus so that the product is kept cool, it is believed that good yields of the free base may be obtained.

Altho the methods thus far described served for the isolation of p phenylenediamine, they were useless for even roughly quantitative work, and since a knowledge of the yields was highly desirable, the possibilities for separating the hydrochloride for this purpose were next investigated.

Beilstein states that the hydrochloride of p phenylenediamine is soluble in alcohol, and since ammonium chloride, the other main product of the reaction, is insoluble in that reagent, a method of separation suggested itself. The method failed because of insufficient solubility of the p. phenylenediamine hydrochloride in alcohol.

A satisfactory method of separation was finally found which is based on the fact that p. phenylenediamine hydrochloride can be precipitated from aqueous solution by saturating the same with hydrochloric acid gas, the ammonium chloride, the copper salt, and most of the other impurities remaining in solution. The method of procedure in general was as follows:

The reddish blue reaction mixture which was obtained by heating p. dichlorobenzene, and ammonia together in the presence of a copper salt was filtered to remove ~~to remove the~~ undecomposed dichlorobenzene and other solid impurities. The filtrate was then steam distilled until all the ammonia was driven off. The distillate was perfectly colorless, but on standing turned to a

deep blue. By extracting it with ether, a bluish ethereal solution was obtained, which yielded a dark resinous oily mass. The amount was too small, however, for identification. The liquid remaining in the flask was allowed to cool, then filtered, and saturated with hydrochloric acid gas. As the solution approached saturation, crystals separated out and soon filled the container. These were filtered off, dried, and weighed. Special details and modifications of this general method will be given in the descriptions of the various experiments.

Altho pure *p*-phenylenediamine hydrochloride is white, the product obtained was generally grey or reddish and gave a dark colored solution. Part of this color may be due to the impurities that result during the reaction, but part is due to the decomposition of the salt itself, for when some of the perfectly white sublimed base was dissolved in concentrated hydrochloric acid reddish black instead of white crystals were obtained.

Attempts to decolorize the salt completely were unsuccessful. Reprecipitation with concentrated hydrochloric acid did not materially affect the color. Recrystallization from alcohol was not feasible because of the relative insolubility of the salt in even hot alcohol. Dilute alcohol (50%) readily dissolved the salt, but the product upon recrystallization from the solvent was still colored. Animal and willow charcoal had no appreciable decolorizing effect; activated charcoal was more efficient and with its use it was possible to obtain a grey product, the yield, however, was poor, probably due to adsorption.

Altho the product could not readily be prepared colorless, it was fairly pure even without recrystallization as the following

analyses show:

Two samples of .3g each of $C_6H_4(NH_2)_2 \cdot 2HCl$ yielded:

AgCl	I. .4675g
	II .4630

Calculated for chlorine:	Found
--------------------------	-------

.1175 g.	I..1153 g.
	II..1145

Sample I was from Run 11 while II was from Run 9. See Table B.

The method of analysis was as follows: The crude product obtained by saturating a solution with hydrochloric acid was dried in warm air, and a portion of this subsequently dried over solid caustic soda in a desiccator for twenty four hours. A sample of the dried salt was mixed with anhydrous sodium carbonate, free from chlorine, and the mixture gently heated. After no more fumes were given off indicating that all of the free base had been removed, the mass was extracted with boiling water, and the insoluble black particles of carbon filtered off. The filtrate was acidified with nitric acid, and the silver chloride precipitated in the usual way. Besides the analyses given, other analyses of the products of the various runs were made and found to give in almost all cases results similar to the ones recorded .

Direct precipitation of the silver chloride from an acid solution of the salt invariably gave slightly high results due to a slight reduction of the excess silver nitrate to metallic silver as indicated by the color of the precipitate.

In the series of experiments on the preparation of p. phenylenediamine which will be taken up now, three factors were studied in particular: temperature, concentration of ammonia, and the pre-

sence of mild reducing agents in conjunction with the copper salt.

Table A.

No.	Concentration of ammonia.	Temp.	Undecomposed $C_6H_4Cl_2$	Actual yield of $C_6H_4(NH_2)_2 \cdot 2HCl$	
1	10%	220 ^o C	7 g.	32 g	65%
2	10	180-190	20	7	14
3	27	205	-	39	80
4	27	200	-	30	61
5	14	210	-	29	60

The reaction mixture in all cases consisted of 40 grams of p.dichlorbenzenä, 240cc of ammonia water (varying strengths as indicated in table), and 5 g. of catalyst which in the first three experiments was cuprous chloride, and in the last two was cuprous iodide. The time of heating was 18 hours except for No. 1 which was heated only 14 hours.

The yields recorded are the yields obtained by saturating the solution with hydrochloric acid gas. It does not include the salt which remained in solution and which by experiment was found to vary from 5-8 grams in 100 cc solution.

Before discussing the results as set down in the table, it is well to discuss the individual experiments, since not all the details can be incorporated in tabular form.

Experiment No. 1. contained iron filings besides the regular reaction mixture, but these did not have any appreciable effect. The reddish violet solution that was obtained was filtered to remove the iron filings and the undecomposed p.dichlorbenzene.

The latter was separated from the iron filings by extraction with ether and then weighing it after the ether was evaporated off. The red solution was neutralized, concentrated to a 200 cc volume, and finally saturated with hydrochloric acid gas, whereupon dark red crystals of p.phenylenediamine hydrochloride separated out. There is a possibility that the product was slightly contaminated with ammonium chloride which also crystallized out because of the high concentration of that compound due to the fact that the large excess of ammonia was not driven off but neutralized directly.

Experiment No.2 was carried out like No.1 except that the solution was steam distilled before it was concentrated and saturated with hydrochloric acid. On concentrating the solution a brick red amorphous precipitate separated out which was filtered off before the solution was neutralized. This precipitate will be discussed later. The product like in No. 1 was colored red.

Experiment No.3 was run the same as No.2 The product was again colored as in the preceding experiments. No amorphous red precipitate was obtained.

Experiment No.4, carried out under practically the same conditions as No.3, yielded a greyish instead of a red product.

Experiment No.5 again yielded a little of the red precipitate referred to under No.2. The product was colored reddish.

Altho it is difficult to draw many definite conclusions from the results given, it appears that the optimum temperature is above 200° , for below this temperature the reaction is incomplete especially with dilute solutions of ammonia.

The concentration of ammonia within certain limits seems to have no marked effect on the yield at the above temperature, but with 5-6% solutions of ammonia, the reaction is very incomplete, even at elevated temperatures. Dilute solutions, furthermore, cause the formation of the red precipitate previously mentioned. The nature of this precipitate was not extensively investigated, but from its general behavior it appears that it is a condensation product. It melts with decomposition above 200° yielding some phenylenediamine, some basic gases, and a charred mass. On exposure to air it undergoes slight oxidation and turns bluish black. It dissolves in water, producing a green solution which turns pink when acidified. It is insoluble in ether but soluble in alcohol and also in concentrated hydrochloric acid. The compound still contains chlorine.

It was observed that when metallic iron was added in the form of iron filings in conjunction with the copper salt, the solution obtained was yellow instead of red, and the product greyish white. This yellow solution, when allowed to stand exposed to the air, slowly turned red. Altho the product was improved in appearance, the reaction was markedly retarded. With powdered aluminum the reaction was completely stopped. The results of a few typical experiments are as follows:

Table B.

No.	Reducing agent.	Conc. of ammonia.	Temp.	Undecomr. $C_6H_4Cl_2$	Yield of $C_6H_4(NH_2)_2 \cdot 2HCl$	
6	Iron filings	16	220°	7	32g.	65% (Impure)
7	"	27	220	10?	7	14
8	"	27	190	10	13	26
9	Activated charcoal.	27	200	0	30	61
10	"	14	200	Tr.	24	49
11	None	14	210	0	26	53

The reaction mixture consisted as usual of 40 grams of p-di-chlorobenzene, 240cc of ammonia water, and 5 grams of catalyst which was cuprous chloride in all cases.

Additional remarks on the experiments are as follows:

Experiment No. 6 has already been described since it appears in Table A as Exp. No. 1.

Experiment No 7. On opening the bomb perfect octohedra crystals were found along the walls and cover. These were colorless but on exposure to the air they quickly turned brown and crumbled. Attempts to reproduce these crystals failed altho experiments under similar conditions were run. The solution was yellow and gave a greyish product.

Experiment No 8. The solution obtained was yellow and yielded a gray product.

Experiment No 9. In this experiment activated charcoal was employed. On opening the bomb the walls were found covered with tiny leaf-

lets of metallic copper. The solution was pale yellow and gave a grayish product.

Experiment No.10. This experiment was the same as No.8 except that a more dilute solution of ammonia was employed. The solution was reddish and gave a red precipitate when it was concentrated. The product was red.

Experiment No 11. This run was the same as No.10.except that no charcoal was added. The solution was red and yielded a colored product.

Again a few general conclusions can be drawn. In concentrated solutions of ammonia certain reducing agents such as iron filings and activated charcoal have a marked favorable effect on the appearance of the final product. The former, however, tends to hinder the reaction, while activated charcoal is free from this objection. These effects were not noticed in dilute ammonia solutions.

Oxidation of p.phenylenediamine.

P.phenylenediamine is readily oxidized to quinone by such oxidizing agents as potassium permanganate or chromic acid. It was observed in this work that even ferric chloride in a hot solution will cause the formation of some quinone as indicated by the quinone odor that is given off. Not only can the base be oxidized to quinone, but it can be directly hydrolyzed to hydroquinone.

²¹ Meyer states that he hydrolyzed the diamine by heating it with a 10% solution of hydrochloric acid at 180° for several hours. In that way he succeeded in getting a 20% yield of hydroquinone, but traces of phenol, aniline, and aminophenol were also formed. He, furthermore states that the higher the temperature the more complete the conversion, but the greater the formation of resinous products.

Since the literature is very meager about the details concerning the oxidation of the diamine, it was that interesting to see how it worked out and what yields could be obtained. Then, too, if the method was found feasible, it might be employed to convert the crude product directly to quinone and so utilize the reaction which has been studied as an indirect method for the preparation of quinone and hydroquinone.

The details of the reaction were as follows: 22 grams of the crude salt were dissolved in 800 cc of a 30% solution of sulphuric acid. This solution was cooled to 5° and while it was stirred, 80 grams of sodium dichromate were added in the course of an hour. The mixture was then packed in ice and allowed to stand over night. The

next morning it was extracted with two 250 cc portions of ether. The ether extract was distilled to remove the ether and the residue sublimed in a current of steam. In this way it was possible to obtain a very pure sample of quinone but the yield was poor, since less than a gram was obtained. No more work was done on that subject, but it seems certain that under proper conditions and with a proper oxidizing agent, a fairly good yield of quinone should be obtained.

It might be added here that the direct hydrolysis of the p. dichlorobenzene by means of dilute sodium hydroxide solution was tried. This experiment was run at a temperature of about 300°. All the dichlorobenzene was decomposed, and the reaction mixture had a decidedly disagreeable odor that resembled that of para cresol. No quinol could be isolated.

Another experiment was carried out using a mixture of sodium hydroxide and ammonium hydroxide plus cuprous chloride. The temperature was maintained a little above 200°. No reaction whatever took place showing that the alkali stops the catalytic action of the copper salt.

The conversion of chlorbenzene into aniline.

The preparation of aniline from chlorbenzene is of greater scientific interest than it is of practical importance. Outside of the patent already mentioned in the introduction no mention of this reaction can be found in the literature.

The object of this work was to find; first, whether aniline was actually produced; secondly, what condition were necessary and what yields were obtainable; and thirdly, whether condensation such as the formation of diphenylamine took place.

The experiments on chlorbenzene like those of p.dichlorbenzene were carried out in the steel bomb at a temperature around 200° . The procedure was simple. The contents of the bomb were acidified and steam distilled whereupon the undecomposed chlorbenzene distilled off. As soon as the distillate was clear, the distillation was stopped, and the mixture allowed to cool. Then it was rendered alkaline with sodium hydroxide and again steam distilled. The aniline came over as a light brown oil, but slight traces of another compound also distilled over which gave to the distillate a blue color. The aniline was extracted with ether and dried over solid sodium hydroxide. The product was fairly pure aniline for almost all of it distilled at 183° . The liquid remaining in the flask was extracted with ether, but the extract yielded nothing, thus showing the absence of diphenylamine, for this compound is non-volatile in steam but soluble in ether. In the experiments as they are listed in Table C one can see that an appreciable amount of chlorbenzene is unaccounted for. Part of the loss may have been

due to failure in not recovering all the aniline and chlorbenzene, but other compounds may have been found which were not isolated.

Table C.

Time of heating: 18 hr.

No.	Ammonia used cc	Strength	Temp.	Undecomp. C_6H_5Cl	Yield of aniline		Catalyst used.
1	150	25%	195°	9	16g.	39%	$CuSO_4$
2	150	27	230	0	16	39	$CuCl$
3	150	27	200	x	13	32	$CuCl$
4	150	14	200	x	14	34	$CuCl$
5	125	27	210	12	13	32	$CuCl$
6	150	27	210	40	0	0	CuI
7	150	14	210	30	0	0	CuI

* 50 grams of chlorbenzene were employed in every experiment.

x. The chlorbenzene was not determined in these two experiments.

From the results as tabulated in the above table one can see that the yield is low. Experiment 1 followed the directions as given in the patent in all particulars except that the time of heating was 18 hours instead of 20. The patent, however, claims an 80% yield, whereas in this experiment it was found that not even half that yield was obtained.

The concentration of ammonia between 14 and 27% seems to have no marked effect. The effect of temperature is greater. In order to bring about a complete decomposition of chlorbenzene, a temperature higher than 200° must be employed, but even then the yield is not increased.

One striking fact is brought out in Experiments No 6 and 7 in

which cuprous iodide is employed as the catalyst. No reaction took place showing that it does not possess catalytic properties either in concentrated or dilute solutions of ammonia.

As has already been mentioned, no diphenylamine could be isolated in these experiments. Since a certain patent previously discussed claims that brombenzene and aniline react in the presence of cuprous iodide to form diphenylamine, it was considered advisable to try it out. The directions were followed, but chlorbenzene was used in place of brombenzene since the latter was not available. A mixture of 30 parts of aniline, an excess of chlorbenzene, and one part of cuprous iodide were heated for 12 hours (the patent calls for 15) with a reflux condenser. The product was bluish in color, but little reaction seems to have taken place and no diphenylamine could be detected.

The next step was to heat a similar mixture under pressure in the steel bomb. This mixture was heated for 18 hours at 220° . Again the mixture was blue. It was steam distilled, and practically all the aniline and chlorbenzene distilled over indicating that little reaction had taken place. The solution was then allowed to cool and was finally extracted with ether. Again no diphenylamine was found.

Summary.

A pressure bomb suitable for heating organic reagents under considerable pressure has been described.

A number of inorganic salts including various salts of copper have been investigated for their effect on labilizing chlorine in p. dichlorbenzene.

P.phenylenediamine has been prepared by the action of ammonia on p.dichlorbenzene in the presence of cuprous salts. The methods used for isolating the free base as well as the hydrochloride have been described.

Quinone has been prepared by the oxidation of p.phenylenediamine.

Aniline has been obtained by the action of ammonia on chlorbenzene in the presence of a copper salt.

An attempt to condense chlorbenzene and aniline in the presence of cuprous iodide has failed.

Conclusion.

Copper salts have a distinct labilizing action on nuclear halogen. The cuprous salts are more effective than the cupric in this respect. The presence of strong reducing agents, oxidizing agents, and alkalies generally retard or entirely stop the reaction.

P.phenylenediamine can readily be prepared by heating p.dichlorbenzene with an excess of either dilute or concentrated ammonia water at about 200° for 20 hours. Dilute solutions at high temperatures cause the formation of a red precipitate, but this does not materially affect the yield. The base can be precipitated as the hydrochloride from the reaction mixture in fairly pure state and with good yields by saturating the solution with gaseous hydrochloric acid.

p-phenylenediamine can be oxidized to quinone, but further study on conditions and oxidizing agents is necessary in order to secure maximum yields.

Aniline is formed from chlorobenzene under conditions similar to those necessary for the preparation of p-phenylenediamine from p-dichlorobenzene, but the reaction is less complete and the yields are poorer. Since the conversion of the p-dichlorobenzene into its respective amino compound thru ammonia takes place much more readily than the conversion of the mono chlor derivative, the second chlorine atom seems to labilize the first one; and when the latter is replaced by an amino group, the remaining halogen atom is markedly labilized since no p-chloraniline can be found as an end product.

The preparation of p-phenylenediamine and aniline from their respective chlor-substituted benzene derivatives are not recorded in chemical literature except in the patents previously mentioned. It has been demonstrated in this work that both these reactions take place and give fairly high yields especially in the case of p-phenylenediamine.

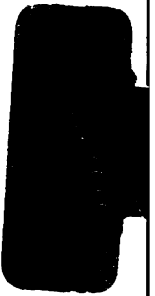
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